

# **EXTRUDABLE HIGHLY CRYSTALLINE THERMOPLASTIC POLYURETHANES**

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## **FIELD OF THE INVENTION**

The present invention relates to thermoplastic polyurethane (TPU) compositions including a crystallization retarding component which advantageously improves processing behavior and allows highly crystalline compositions to be processed in an extruder. The crystallization retarding component is generally present in the polyurethane composition in amounts sufficient to reduce crystal formation during the extrusion process and essentially delay crystallization onset until the composition has exited an extruder die or outlet, without altering the desirable properties of the final product. The crystallization retarding components comprise short chain or monomeric diols which are branched, substituted, or contain heteroatoms.

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## **BACKGROUND OF THE INVENTION**

Typically, highly crystalline, phase separated thermoplastic polyurethanes have not been utilized in extrusion applications as the compositions are generally difficult to process or even unprocessable as they crystallize and form conglomerates or chunks of solid matter in the extrusion process equipment. Furthermore, attempts to prevent crystallization by increasing the processing temperatures of the extrusion equipment have been unsuccessful and result in heat-decomposed products.

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Highly crystalline thermoplastic polyurethane (TPU) products with desirable properties for extrusion have heretofore generally been unavailable. Thermoplastic polyurethanes with high crystallinity have stronger wear resistance and solvent resistance than their relatively low crystalline counterparts.

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Highly crystalline thermoplastic polyurethanes also set up faster during extrusion process making the extruded shapes such as hose, tube, sheets, films, fibers and profiles easier to handle after

the polymer melt exits the shaping die. This is desirable because it leads to increased productivity and better final product quality.

## **SUMMARY OF THE INVENTION**

5           The present invention relates to extruded thermoplastic polyurethane compositions having high crystallinity. Advantageously, the thermoplastic polyurethane includes a crystallization delaying or  
10           retarding component that allows the compositions to be easily extruded without causing appreciable solid or crystallization buildup in an extruder. Advantageously, the crystallization retarding component shifts or lowers the crystallization temperature of a composition when compared to the same composition without the crystallization retarding component.

15           Generally, highly crystalline thermoplastic polyurethanes contain a relatively high amount of hard segments. Crystallinity is desired because it enhances the mechanical properties, chemical resistance and heat resistance of the final product. The low levels of crystallization retarding component still allow crystallization of hard  
20           blocks to proceed but at a much slower rate than without the same. Thus desirable polymer properties are still retained. The slower crystallization rate in turn does not permit the formation of crystalline solid matter or chunks to build up in the extruder. High quality extruded crystalline products such as films, sheets, or tubing, etc., can  
25           be obtained.

## **BRIEF DESCRIPTION OF THE DRAWINGS**

FIGS. 1 through 8 illustrate graphs produced by a differential scanning calorimeter (DSC) for various polyurethane formulations as  
30           set forth in the Example section.

FIGS. 9 through 16 illustrate melt viscosity curves for various polyurethane formulations as set forth in the Example section.

## DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic polyurethanes of the present invention have a high crystalline content and include a crystallization retarding component, such as dipropylene glycol, which allows the compositions to be extruded and processed into useful products.

The crystallization temperature of the composition can typically be determined by differential scanning calorimetry. Generally, crystallized compositions can be melted, solvated, or otherwise amorphized and then recrystallized. The term crystallizable refers to compositions that are a) crystallized or b) uncrystallized, but capable of crystallization by a reduction in temperature of the composition.

Highly crystalline or high crystalline content refers to thermoplastic polyurethane compositions which contain at least about 20%, 25%, 30% or 40% of hard segment content up to about 70%, 80%, 90%, 95%, or even 100%. Hard segment content can be defined as equal to the total of the weight percent of the isocyanate component, chain extenders, and crystallization retarding component divided by the total weight percent of the thermoplastic polyurethane composition (weight percent of isocyanate component, chain extender, crystallization retarding component, and polyol component). It is known that not all highly crystalline polymers fall within the above-defined range of hard segments, but the same are to be included within the scope of the invention. Highly crystalline thermoplastic urethanes are those which readily crystallize during the extrusion process in an extruder. Their crystallinity can also be quantified by those of ordinary skill in the art by typical DSC scans, for example as shown in Figure 1 through Figure 8 hereinbelow. Compositions that show greater than generally about 4, desirably about 4.5, and preferably about 5 or 5.5 up to about 20, 25, 30 or 40 J/g heat of crystallization exotherm, as calculated by ASTM test D3417-99, (third curve of each DSC graph) during cool down from melt can be described as highly crystalline.

Thermoplastic polyurethane composition refers to a composition containing polyurethane, reagents used to form the

polyurethane, or a combination thereof and can refer to the composition prior to extrusion, within the extruder, or after extrusion.

The thermoplastic polyurethanes of the present invention are generally prepared by combining and reacting a) a polyol component of at least one hydroxyl terminated intermediate such as hydroxyl terminated polyester, polyether, polycarbonate, or polycaprolactone with b) at least one polyisocyanate component, c) a crystallization retarding component, d) at least one primary chain extender and optionally, a catalyst. These reactants generate a thermoplastic polyurethane in, for example, an extruder or other reaction vessel.

The components of the high crystalline content polyurethane composition can be combined to form the polyurethane composition prior to introduction into the extruder or they can be combined *in situ* within the extruder. The crystallization retarding component is typically provided in an amount sufficient to produce less build-up of crystallized polyurethane or solid matter in the extruder than would be found using the same polyurethane composition without the crystallization retarding component. For purposes of this comparison, the amount of build-up for a given amount of material that has been extruded can be determined in a variety of ways including, for example, comparing the thickness of the build-up, the surface area of the extruder covered by the build-up, and/or the weight of the build-up for a given amount of polyurethane composition extruded at the same conditions. For example, for a given extruder, extruder configuration, extrusion conditions (e.g., extrusion temperature(s), pressure(s), and speed(s), and period of time, the addition of a crystallization retarding component can reduce the build-up by at least 90%. Extrusion conditions and amounts of crystallization retarding component can be chosen so that build-up can be reduced generally by at least 95%, and even by at least 98%, 99%, or more. In at least some instances, the addition of a crystallization retarding component can prevent, i.e. reduce by about 100%, what would otherwise be significant, build-up for a given set of conditions and period of time. The specified percentage of reduction in build-up is achieved if there is the

appropriate reduction in build-up according to at least one measurement criterion, even if that reduction percentage is not met when using another measurement criteria.

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## **Polyols**

The thermoplastic polyurethanes of the present invention include a polyol component, which include but are not limited to hydroxyl terminated polyesters, hydroxyl terminated polyethers,  
10 hydroxyl terminated polycarbonates, hydroxyl terminated polycaprolactones and hydroxyl terminated polyolefins.

The class of hydroxyl terminated polyesters are generally polyesters, often linear polyesters, having a number average molecular weight,  $M_n$ , of at least 500 and typically no more than  
15 10,000 to provide the polyurethane with a distribution of hard and soft segments. The number average molecular weight of the hydroxyl terminated polyester is typically in the range of about 700 to about 5,000, and often is in the range of about 700 to about 4,000.

The number average molecular weight can be determined, for example, by assay of the number of terminal functional groups for a  
20 given weight of polymer. Suitable hydroxyl terminated polyesters generally have an acid number of 1.3 or less and typically 0.8 or less. The acid number refers to the number of milligrams of potassium hydroxide needed to neutralize one gram of the hydroxyl terminated polyester. Suitable hydroxyl terminated polyesters are commercially  
25 available from companies such as, for example, Witco Corp. of Perth Amboy, NJ as Fomrez, Inolex Chemical Co. of Philadelphia, PA as Lexorez, and Ruco Polymer Corp. of Hicksville, NY as Rucofeld.

The hydroxyl terminated polyester polymers can be produced  
30 by, for example, (1) an esterification reaction of one or more dicarboxylic acids or anhydrides using one or more glycols or (2) a transesterification reaction of one of more esters of dicarboxylic acids using one or more glycols. Mole ratios generally in excess of more than one mole of glycol to acid, anhydride, or ester are preferred so as

to obtain linear chains having a preponderance of terminal hydroxyl groups.

Suitable dicarboxylic acids for preparing a hydroxyl terminated polyester intermediate include aliphatic, cycloaliphatic, and aromatic dicarboxylic acids. A single dicarboxylic acid or a combination of dicarboxylic acids can be used. Typically, the dicarboxylic acids have a total of from 4 to about 15 carbon atoms. Examples of suitable dicarboxylic acids include succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, dodecanedioic, isophthalic, terephthalic, and cyclohexane dicarboxylic acids, and the like. Anhydrides of the above dicarboxylic acids, such as phthalic anhydride, tetrahydrophthalic anhydride, and the like, can also be used. Adipic acid is a commonly used dicarboxylic acid.

If the transesterification route for formation of the hydroxyl terminated polyester is utilized, esters of the dicarboxylic acids described above can be used. These esters typically include an alkyl group, usually having 1 to 6 carbon atoms, in place of the acidic hydrogen of the corresponding acid functionalities.

The glycols which are reacted to form the hydroxyl terminated polyester intermediate can be aliphatic, aromatic, or combinations thereof. The glycols typically have a total of from 2 to 12 carbon atoms. Suitable glycols include, for example, ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and the like. Commonly used glycols are 1,4-butanediol and 1,6-hexanediol.

The class of hydroxyl terminated polyether polyols are derived from a diol or polyol having a total of from 2 to about 15 carbon atoms. For example, an alkyl diol or glycol can be reacted with an ether, such as an alkylene oxide having from 2 to 6 carbon atoms. Suitable alkylene oxides include, for example, ethylene oxide, propylene oxide, or mixtures thereof. Suitable hydroxyl terminated polyethers are commercially available from companies such as, for

example, E. I. DuPont de Nemours Co., Inc. of Wilmington, DE as Terathane, BASF Corp. of Parsippany, NJ as poly THF and Penn Specialties of Philadelphia, PA as Polymeg.

5        Suitable polyether polyols include, for example, poly(ethylene glycol) which can be formed by reacting ethylene oxide with ethylene glycol, poly(propylene glycol) which can be formed by reacting propylene oxide with propylene glycol, poly(propylene-ethylene glycol) which can be formed by reacting propylene oxide and ethylene oxide with propylene glycol, poly(tetramethylene glycol) (PTMG) which can be formed by reacting water with tetrahydrofuran (THF). Other  
10        suitable polyether polyols include polyamide adducts of an alkylene oxide including, for example, ethylenediamine adduct which is the reaction product of ethylenediamine and propylene oxide, diethylenetriamine adduct which is the reaction product of  
15        diethylenetriamine with propylene oxide, and similar polyamide type polyether polyols. Co-polyethers can also be utilized in the current invention. Typical co-polyethers include the reaction product of THF and ethylene oxide or THF and propylene oxide. Suitable co-polyethers are available from BASF Corp. of Parsippany, N. J. as Poly  
20        THF B, a block copolymer, and poly THF R, a random copolymer.

      Suitable hydroxyl terminated polyether intermediates generally have a number average molecular weight as determined by assay of the terminal functional groups, of at least 500 and typically no more than 10,000 to produce a desired ratio of soft and hard segments of  
25        the polyurethane. Typically, the number average molecular weight of the hydroxyl terminated polyether ranges from about 500 to about 5,000. Often the number average molecular weight of the hydroxyl terminated polyether ranges from about 700 to about 3,000.

      The class of hydroxyl terminated polycarbonates are  
30        commercially available from Stahl USA of Peabody, MA. Suitable hydroxyl terminated polycarbonates can be prepared by reacting a glycol with a carbonate. U. S. Patent No. 4,131,731, incorporated herein by reference, describes hydroxyl terminated polycarbonates, their preparation and how they can be utilized. Such polycarbonates

are typically linear. The number average molecular weight of the hydroxyl terminated polycarbonates is generally at least about 500 and typically not more than 3,000.

5 The class of hydroxyl terminated polycaprolactones are commercially available from companies such as, for example, Union Carbide Corp. of Danbury, CT. Hydroxyl terminated polycaprolactones can be formed by reaction of a caprolactone with a glycol. Suitable caprolactones include  $\epsilon$ -caprolactone and methyl  $\epsilon$ -caprolactone. Suitable glycols include, for example, ethylene glycol,  
10 1,2-propanediol, 1,3-propanediol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2-dimethyl-1,3-propanediol, 1,4-cyclohexanedimethanol, decamethylene glycol, dodecamethylene glycol, and the like. Methods for the preparation of hydroxyl terminated polycaprolactones are generally known to those of ordinary  
15 skill in the art.

The hydroxyl terminated polyolefins are prepared from olefin monomers having from 4 to about 10 or 12 carbon atoms such as butadiene. The number average molecular weight of the hydroxyl terminated polyolefins range from about 500 to about 6,000 or 10,000.  
20 The hydroxyl terminated polyolefins are available from Shell as Kraton Liquid L and Mitsubishi Chemical as Polytail H.

The polyol component such as the polyether polyols of the present invention have an unsaturation content of generally less than 0.10 or 0.05 meq/gram, desirably less than about 0.02 or 0.03  
25 meq/gram and preferably less than about 0.015 meq/gram, (milliequivalents per gram) per polyol, as can be determined by methods well known to those skilled in the art. The number average molecular weight of the polyol component of the present invention, which can comprise different polyols as defined above, is generally  
30 from about 500 or 600 to about 10,000, desirably from about 700 to about 5,000, and preferably from about 1,000 to about 4,000 per polyol. The average hydroxyl functionality of the polyol component is generally from about 1.8 to about 2.2, desirably from about 1.90 to about 2.10, and preferably from about 1.95 to about 2.00 or 2.05. The



polyol component is utilized in the thermoplastic polyurethane composition of the present invention in amounts so that the hydroxyl group content is generally from about 2 to about 70 equivalents, desirably from about 3 to about 65 equivalents, and preferably from about 5 or 10 to about 50 or 60 equivalents per 100 equivalents of the total hydroxyl groups present in the thermoplastic polyurethane composition.

### **Polyisocyanates**

The polyurethanes of the present invention are derived from an isocyanate compound. In order to form large linear polyurethane chains, di-functional or polyfunctional isocyanates are utilized, with diisocyanates being preferred. Suitable polyisocyanates are commercially available from companies such as, but not limited to, Bayer AG of Leverkusen, Germany as Mondur, The BASF Corporation of Parsippany, New Jersey as Lupriate, The Dow Chemical Company of Midland, Michigan as Isonate, and Huntsman Chemical of Utah as Rubinate. The polyisocyanates of the present invention generally have a formula  $R(NCO)_n$ , where  $n$  is usually an integer of 2 to 4 and preferably about 2 being preferred.  $R$  can be an aromatic, cycloaliphatic, an aliphatic, or combinations thereof having from 2 to 20 carbon atoms. Examples of polyisocyanates include, but are not limited to diphenylmethane-4,4'- diisocyanate (MDI); toluene-2,4-diisocyanate (TDI); toluene-2,6-diisocyanate (TDI); methylene bis (4-cyclohexylisocyanate ( $H_{12}$  MDI); 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexyl isocyanate (IPDI); 1,6-hexane diisocyanate (HDI); naphthalene-1,5-diisocyanate (NDI); 1,3- and 1,4-phenylenediisocyanate; triphenylmethane-4,4',4"- triisocyanate; polyphenylpolymethylenepolyisocyanate (PMDI); m-xylene diisocyanate (XDI); 1,4-cyclohexyl diisocyanate (CHDI); isophorone diisocyanate; isomers and mixtures or combinations thereof. The preferred isocyanates are aromatic, and include

diphenylmethane-4,4'-diisocyanate (MDI), including polymeric MDI, and also H<sub>12</sub> MDI which produces polyurethanes with low yellow color.

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### **Crystallization Retarding Component**

A crystallization retarding component is added to the high crystalline content thermoplastic polyurethanes of the present invention in sufficient amounts to allow the composition to be extruded. That is, while not being bound by theory, it is thought that the crystallization retarding component delays the formation of the crystalline structures for a sufficient amount of time to allow the composition to be processed by extrusion. The onset of crystallization is delayed so that preferably 100% of crystallization occurs after processing of the thermoplastic polyurethane in the extruder, i.e. after the composition leaves or exits the extruder die or orifice.

The crystallization retarding component advantageously lowers or shifts the crystallization temperature of a thermoplastic polyurethane composition when compared to the same compositions without the crystallization retarding component, advantageously allowing the previously unextrudable highly crystallization compositions to be processed in an extruder. The crystallization retarding components are generally sterically hindered so that crystalline formation is interrupted or delayed allowing the thermoplastic polyurethane to be processed. The crystallization retarding components are short chain or monomeric diols which are branched, substituted and/or contain heteroatoms (atoms other than carbon). If the crystallization retarding component is an aromatic containing diol, the substitution must be other than trans substitution, i.e. there can be substantially no trans-isomers, preferably so that at least some steric hindrance exists in the diol.

Crystallization retarding components include, but are not limited to, dipropylene glycol, tripropylene glycol, diethylene glycol, triethylene glycol, cis-trans-isomers of cyclohexyl dimethylol,

neopentyl glycol and substituted alkane diols such as 1,3-butane diol, and 2-methyl-2,4-pentane diol, with dipropylene glycol being preferred. Any branched or substituted alkane diols having from about 2 up to about 12 carbon atoms in the main chain can be utilized. Substituents include alkyl groups, cyclohexyl groups, aryl groups and halogen atoms such as chlorine and bromine.

The crystallization retarding component is utilized in the thermoplastic polyurethane composition of the present invention in amounts so that the hydroxyl group content is generally from about 1 to about 15 or 20 equivalents, desirably from about 2 or 3 to about 15 equivalents, and preferably from about 5 to about 11 or 12 equivalents, per 100 equivalents of the total hydroxyl groups, i.e. from the polyol component, crystallization retarding component, and the chain extending component present in the polyurethane composition. The crystallization retarding components should preferably react at a similar rate as the primary or main chain extenders such as 1,4-butane diol. The molecular weight range for the crystallization retarding component is less than about 450 or 500 number average.

### **Chain Extenders**

Chain extenders are desirably employed in the polyurethane formulations of the present invention generally to increase the molecular weight thereof, and are well known to the art and to the literature. They are also responsible for formation of crystalline hard blocks leading to thermoplastic polyurethanes with desirable mechanical properties. Suitable chain extenders are unbranched, unsubstituted, straight chain alkane diols free of heteroatoms which have a total from about 2 to about 6 carbon atoms. Examples include ethanediol, 1,6-hexanediol, 1,3-propanediol, 1,5-pentanediol and preferably 1,4-butanediol. Suitable chain extenders also include high (trans-trans-)isomers (greater than at least 60%, 75%, 90% or 95%) of substantially non-sterically hindered aromatic glycols such as 1,4-

benzenedimethylol benzene glycol, 1,4-cyclopentanediol, and the like. Still other suitable chain extenders are aromatic-aliphatic glycols such as 1,4 *bis*(2-hydroxyethoxy) benzene (HQEE), and high trans-trans-isomer containing cycloaliphatic glycols such as 1,4-cyclohexanedimethanol (CHDM). Mixtures of the above noted chain extenders can also be utilized.

The preferred chain extenders of the present invention include 1,4-butanediol, ethylene glycol, 1,6-hexane diol, 1,4-cyclohexanedimethanol (CHDM), 1,4 *bis*(2-hydroxyethoxy) benzene (HQEE), 1,4-benzenedimethylol, 1,3-propane diol, and 1,5-pentane diol. The amount of the one or more chain extenders utilized is based upon the total equivalents of the hydroxyl groups of the reactive components of the thermoplastic polyurethane composition. The amount of chain extender utilized generally is wherein the hydroxyl group content is from about 5 or 10 to about 97 or 99 equivalents, desirably from about 20 to about 95 equivalents, and preferably from about 30 or 40 to about 90 equivalents based on the 100 equivalents of the total hydroxyl groups present in the polyurethane composition.

The equivalent weight ratio of polyisocyanate functional groups to total hydroxyl functional groups of the polyol component, crystallization retarding component, and chain extender is generally from about 0.90 to about 1.10, desirably from about 0.95 to about 1.05, and preferably from about 0.98 to about 1.03.

### **Catalysts**

Catalysts are optionally, but preferably used in the polyurethane reaction mixtures of the present invention. Any of the catalysts conventionally employed or known in the art and to the literature to catalyze the reaction of an isocyanate with a reactive hydrogen containing compound can be employed for this purpose. Such catalysts include organic and inorganic acid salts of, and organometallic derivatives of, bismuth, tin, iron, antimony, cobalt, thorium, aluminum, zinc, nickel, cerium, molybdenum, vanadium, copper, manganese and zirconium, as well as phosphines and tertiary

organic amines. Representative organotin catalysts include stannous octoate, dibutyltin dioctoate, dibutyltin diluarate, and the like. Representative tertiary organic amine catalysts include triethylamine, triethylenediamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetraethylethylenediamine, N-methylmorpholine, N-ethylmorpholine, N,N,N',N'-tetramethylguanidine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N-dimethylethanolamine, N,N-diethylethanolamine, and the like.

The amount of catalyst employed is generally within the range of about 20 to about 500 parts by weight per million parts by weight of the total weight of the polyisocyanate(s), polyol component, and chain extender(s). Mixtures of the above noted catalysts can likewise be utilized. It is desirable to use minimal amounts of the catalyst in order to minimize side reactions. Preferred catalysts include stannous octoate, dibutyltin dioctoate, and dibutyltin diluarate and bismuth octoate.

In addition to the above-identified components, the polyurethane compositions of the present invention can also contain various additives, pigments, dyes, fillers and the like, utilized in conventional amounts which are well known to the art and to the literature.

Generally additives are utilized which impart desired properties to the thermoplastic polyurethanes such as various antioxidants, various ultraviolet light inhibitors, waxes such as amide waxes and ester waxes, thickening agents, and the like. The fillers, when utilized, are generally mineral fillers, that is inorganic, and include ground mica, talc, kaolin clay, calcium carbonate, calcium sulfite, colloidal silica, fumed silica, wollastonite, hollow glass microspheres, glass, carbon and graphite fibers, various metallic oxides such as zinc, titanium zirconium, and the like, ground quartz, various metallic silicates, metallic powders such as lead, aluminum, bronze, and the like.

If it is desired that the polyurethane composition of the present invention have a color or hue, any conventional pigment or dye can be utilized in conventional amounts. Hence, any pigment known to the

art and to the literature can be utilized as for example titanium dioxide, iron oxide, carbon black, and the like, as well as various dyes provided that they do not interfere with the various urethane reactions.

5 The thermoplastic polyurethane elastomers of the invention can be prepared by processes which are conventional in the art for the synthesis of polyurethane elastomers such as but not limited to a two-step prepolymer process or preferably, a one-shot (master batch) technique. In the two-step process, the prepolymer is formed by reacting the polyol component with the polyisocyanate component to  
10 form an isocyanate terminated prepolymer which is subsequently chain extended. In the preferred one-shot procedure, all of the reactants are brought together and simultaneously or substantially simultaneously reacted. The one-shot procedure is preferably performed in an extruder, e.g. single screw, twin screw (desired),  
15 wherein the formative components, i.e. the polyol(s), the polyisocyanate(s), and the chain extender(s), the catalyst(s), and any other additives, etc., if desired, are introduced individually or as a mixture into the extruder, and reacted at a temperature generally from about 100°C to about 300°C, desirably from about 150°C to about 250°C, and preferably from about 150°C to about 240°C.  
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The resulting polyurethanes of the present invention have a weight average molecular weight generally from about 50,000 to about 500,000, desirably from about 75,000 to about 250,000, and preferably from about 100,000 to about 150,000, measured by gel  
25 permeation chromatography against polystyrene standards. The polyurethanes generally have a hardness which ranges from about 65 Shore A to about 80 D or even harder.

The resulting high crystalline content thermoplastic polyurethane can be extruded into any desired end product or form, or  
30 can be cooled and granulated for storage or bulk shipping. The extrudate can also be immediately further processed to give a desired final end-use product.

The high crystalline content thermoplastic polyurethanes of the present invention advantageously are suitable for many applications, including, but not limited to, membranes, breathable films or sheets which can be utilized for house wrap, roofing materials or membranes, tubing, wire and cable jacketing, molded parts, shoe soles, hoses, films for lamination, waistbands, and elastic structures such as fibers.

The present invention will be better understood by reference to the following examples which serve to illustrate the invention, but not to limit the same.

### Examples

The following examples confirm the dramatic effect of the crystallization retarding components on the melt stability of the TPUs. The compositions listed hereinbelow were tested under dynamic conditions (100 radian/second frequency) with a parallel plate melt viscometer according to ASTM D4440-95a over a period of two hours.

Example 1: No crystallization retarding component; 31.2% hard segment content.

#### Example 1

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	2.93	366.64	25.08
Butane diol (chain extender)	45.06	1.92	86.56	5.92
DPG Dipropylene Glycol (cyc)	67.09	0.00	0.00	0.00
PTMEG 2000 (polyol)	1000.00	1.00	1000.00	68.40
TOTAL OH		2.92	1086.56	74.32
TOTAL OH & NCO			1453.20	99.40
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate (catalyst)			0.07	0.01
IRGANOX 1010			4.39	0.30
Tinuvin 328			4.39	0.30
TOTAL ADDITIVES			8.85	0.61
TOTAL FOR THE RUN			1462.04	100.00

FIG. 9 illustrates a graph of viscosity data calculated from the Example 1 polyurethane formulation. This composition is a TPU of hardness 75 A. With no crystallization retarding component, the complex melt viscosity,  $\eta^*$  (Pa-sec), gradually increased over the test period of 2 hrs due to the flow restrictions imposed by the

crystallization of the hard blocks. The product of this nature is expected to gradually freeze in dead spots of an extruder into solid crystalline structure parts of which will then be release into the melt stream from time to time during the course of the extrusion, spoiling the quality of the extrudate like films, tubing etc. G' is the elastic component of the viscosity and G'' is the viscous component of the viscosity.

Example 2: 10 Equivalents of Crystallization Retarding Component, Hard Segment Content 31.6%.

#### Example 2

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	2.9410	368.21	24.967
Butane diol (chain extender)	45.06	1.6469	74.21	5.032
DPG Dipropylene Glycol (cnc)	67.09	0.2941	19.73	1.338
PTMEG 2000 (polyol)	1000.00	1.0000	1000.00	67.808
TOTAL OH		2.9410	1093.94	74.178
TOTAL OH & NCO			1462.15	99.145
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate (catalyst)			0.07	0.005
Acrawax C			3.69	0.250
IRGANOX 1010			4.42	0.300
Tinuvin 328			4.42	0.300
TOTAL ADDITIVES			12.61	0.855
TOTAL FOR THE RUN			1474.76	100.00

FIG. 10 illustrates a graph of viscosity data calculated from the Example 2 polyurethane formulations. The same test of the same hardness TPU made by replacing 10 % of equivalent weight of main chain extender 1,4 butane diol (BDO) with dipropylene glycol (DPG). The test clearly shows that the complex melt viscosity is flatter and does not rise significantly during the course of the test. This indicates good extrusion processability. To confirm the indicated extrudability, the TPU formulation was scaled up on a pilot reactor (40 mm twin screw Werner Pflidere extruder) and extruded into excellent quality blown film on a 2 ½" single screw Killion extruder.



Example 3: 0 Equivalents of Crystallization Retarding  
Component, Hard Segment Content 65.1%.

Example 3

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	6.9321	867.89	50.040
Butane diol (chain extender)	45.06	5.6321	253.78	14.632
PTMEG 1000 (polyol)	500.00	1.0000	500.00	28.828
PTMEG 650 (polyol)	335.00	0.3000	100.50	5.794
DPG Dipropylene Glycol (cnc)	67.09	0.0000	0.00	0.000
TOTAL OH		6.9321	854.28	49.255
TOTAL OH & NCO			1722.18	99.295
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate (catalyst)			0.09	0.005
IRGANOX 1010			6.94	0.400
Tinuvin 328			5.20	0.300
TOTAL ADDITIVES			12.23	0.705
TOTAL FOR THE RUN			1734.40	100.00

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FIG. 11 illustrates a graph of viscosity data calculated from the Example 3 polyurethane formulation. FIG. 11 shows the melt stability of a highly crystalline 65 Shore D hard ether. Rapid increase in complex melt viscosity indicates this product is not suitable for extrusion process. Attempts to extrude this product resulted in significant solidification in die and flight channels of the extruder screw.

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Example 4: 15 Equivalents of Crystallization Retarding  
Component, Hard Segment Content 66.6%.

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Example 4

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	7.2115	902.88	50.040
Butane diol (chain extender)	45.06	4.8298	217.63	12.062
PTMEG 1000 (polyol)	498.00	1.0000	498.00	27.601
PTMEG 650 (polyol)	335.00	0.3000	100.50	5.570
DPG Dipropylene Glycol(cnc)	67.09	1.0817	72.57	4.022
TOTAL OH		7.2115	888.70	49.255
TOTAL OH & NCO			1791.59	99.295
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate (catalyst)			0.09	0.005
IRGANOX 1010			7.22	0.400
Tinuvin 328			5.41	0.300
TOTAL ADDITIVES			12.72	0.705
TOTAL FOR THE RUN			1804.31	100.00

FIG. 12 illustrates a graph of viscosity data calculated from the Example 4 polyurethane formulation. FIG. 12 shows the melt stability of the similar ether product of Example 3 modified with 15 equivalents of dipropylene glycol (DPG). The increase in melt viscosity is mild and gradual. This material was extruded successfully into tubing and sheets on a 2 ½" Killion extruder.

Example 5: 0 Equivalents of Crystallization Retarding Component, Hard Segment Content 58.9%.

Example 5

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	13.1205	1642.69	43.789
BDO (chain extender)	45.06	12.1205	546.15	14.559
Ester Polyol (polyol)	1525.00	1.0000	1525.00	40.652
TOTAL OH		13.1205	2071.15	55.211
TOTAL OH & NCO			3713.84	99.000
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			9.38	0.250
IRGANOX 1010			9.38	0.250
Stabaxol P-200			18.76	0.500
TOTAL ADDITIVES			37.51	1.000
TOTALS FOR THE RUN			3751.36	100.000

FIG. 13 illustrates a graph of viscosity data calculated from the Example 5 polyurethane formulation. FIG. 13 shows the melt curves of a highly crystalline 55 D ester polyol based TPU. The rapid increase in viscosity due to crystallization exceeds the capacity of the viscometer machine to complete the test after 25 minutes. This product could not be extruded in an extruder.

Example 6: 10 Equivalents of Crystallization Retarding Component, Hard Segment Content 59.7%.

### Example 6

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	13.382	1675.40	43.811
BDO (chain extender)	45.06	11.044	497.62	13.013
Ester Polyol (polyol)	1525.00	1.000	1525.00	39.878
Dipropylene Glycol DPG(crc)	67.09	1.338	89.78	2.348
TOTAL OH		13.382	2112.40	55.239
TOTAL OH & NCO			3787.80	99.050
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			7.65	0.200
IRGANOX 1010			9.56	0.250
Stabaxol P-200			19.12	0.500
TOTAL ADDITIVES			36.33	0.950
TOTALS FOR THE RUN			3824.13	100.000

FIG. 14 illustrates a graph of viscosity data calculated from the Example 6 polyurethane formulation. The melt curves shown in FIG. 14 is the ester product of Example 5 modified with 10 equivalents of dipropylene glycol (DPG). This product was successfully extruded into tubing on a 2 ½" Killion extruder.

Example 7: 0 Equivalents of Crystallization Retarding Component, Hard Segment Content 48.4%.

### Example 7

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	13.1225	1642.94	39.938
BDO (chain extender)	27.19	12.1225	329.62	8.013
Ester Polyol (polyol)	2100.00	1.0000	2100.00	51.049
Dipropylene Glycol DPG (crc)	67.09	0.0000	0.00	0.000
TOTAL OH		13.1225	2429.62	59.062
TOTAL OH & NCO			4072.55	99.000
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			10.28	0.250
IRGANOX 1010			10.28	0.250
Stabaxol P-200			20.57	0.500
TOTAL ADDITIVES			41.14	1.000
TOTALS FOR THE RUN			4113.69	100.000

FIG. 15 illustrates a graph of viscosity data calculated from the Example 7 polyurethane formulation. FIG. 15 shows the melt viscosity curve of an unmodified highly crystalline ester of 50 D

hardness. As in earlier comparisons the product in chart 7 was not extrudable whereas the modified product in FIG. 16 generated from the polyurethane formulation of Example 8 extrudes easily.

- 5                      Example 8: 10 Equivalents of Crystallization Retarding Component, Hard Segment Content 54.6%.

Example 8

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	14.9032	1865.88	39.938
BDO (chain extender)	45.06	12.4129	559.32	11.972
Ester Polyol (polyol)	2100.00	1.0000	2100.00	44.950
Dipropylene Glycol DPG (cnc)	67.09	1.4903	99.99	2.140
TOTAL OH		14.9032	2759.31	59.062
TOTAL OH & NCO			4625.19	99.000
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			11.68	0.250
IRGANOX 1010			11.68	0.250
Stabaxol P-200			23.36	0.500
TOTAL ADDITIVES			46.72	1.000
TOTALS FOR THE RUN			4671.91	100.000

- 10                      The following compositions were analyzed by DSC to illustrate the effect of the crystallization composition of the present invention.

- 15                      Formulation for Figure 1 (DSC), No Crystallization Retarding Component

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	13.1205	1642.69	43.789
BDO (chain extender)	45.06	12.1205	546.15	14.559
Ester Polyol (polyol)	1525.00	1.0000	1525.00	40.652
Dipropylene Glycol DPG (cnc)	0.00	0.0000	0.00	0.000
TOTAL OH		13.1205	2071.15	55.211
TOTAL OH & NCO			3713.84	99.000
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			9.38	0.250
IRGANOX 1010			9.38	0.250
Stabaxol P-200			18.76	0.500
TOTAL ADDITIVES			37.51	1.000
TOTALS FOR THE RUN			3751.36	100.000

Formulation for Figure 2 (DSC), 10 Equivalents of  
Crystallization Retarding Components per 100 OH Equivalents

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	13.382	1675.40	43.811
BDO (chain extender)	45.06	11.044	497.62	13.013
Ester Polyol (polyol)	1525.00	1.0000	1525.00	39.878
Dipropylene Glycol DPG (crc)	67.09	1.338	89.78	2.348
TOTAL OH		13.382	2112.40	55.239
TOTAL OH & NCO			3787.80	99.050
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			7.65	0.200
IRGANOX 1010			9.56	0.250
Stabaxol P-200			19.12	0.500
TOTAL ADDITIVES			36.33	0.950
TOTALS FOR THE RUN			3824.13	100.000

5 Formulation for Figure 3 (DSC), No Crystallization Retarding  
Component

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	3.4965	437.77	41.430
BDO (chain extender)	45.06	2.4965	112.49	10.646
PTMEG 1000	500.00	1.0000	500.00	47.319
Dipropylene Glycol DPG (crc)	67.09	0.0000	0.00	0.000
TOTAL OH		3.4965	612.49	57.965
TOTAL OH & NCO			1050.26	99.395
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate			0.05	0.005
IRGANOX 1010			3.17	0.300
Tinuvin 328			3.17	0.300
TOTALS FOR THE RUN			1056.65	100.000

10 Formulation for Figure 4 (DSC), 8.8 Equivalents of  
Crystallization Retarding Components per 100 OH Equivalents

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	3.6856	461.44	42.187
Butane diol (chain extender)	45.06	2.3529	106.02	9.693
PTMEG 1000 (polyol)	498.00	1.0000	498.00	45.530
Dipropylene Glycol DPG (crc)	67.09	0.3235	21.71	1.984
TOTAL OH		3.6764	625.73	57.208
TOTAL OH & NCO			1087.17	99.395
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate (catalyst)			0.05	0.005
IRGANOX 1010			3.28	0.300
Tinuvin 328			3.28	0.300
Total Nonreactants			6.62	0.605
TOTAL FOR RUN			1093.78	100.000

Formulation for Figure 5 (DSC), No Crystallization Retarding  
Component=0 Equivalents

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	13.1225	1642.94	39.938
BDO (chain extender)	27.19	12.1225	329.62	8.013
Ester Polyol (polyol)	2100.00	1.0000	2100.00	51.049
Dipropylene Glycol DPG (crc)	67.09	0.0000	0.00	0.000
TOTAL OH		13.1225	2429.62	59.062
TOTAL OH & NCO			4072.55	99.000
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			10.28	0.250
IRGANOX 1010			10.28	0.250
Stabaxol P-200			20.57	0.500
			41.14	1.000
Totals for Run			4113.69	100.000

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Formulation for Figure 6 (DSC), 10 Equivalents of  
Crystallization Retarding Components per 100 OH Equivalents

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	14.9032	1865.88	39.938
BDO (chain extender)	45.06	12.4129	559.32	11.972
Ester Polyol (polyol)	2100.00	1.0000	2100.00	44.950
Dipropylene Glycol DPG (crc)	67.09	1.4903	99.99	2.140
TOTAL OH		14.9032	2759.31	59.062
TOTAL OH & NCO			4625.19	99.000
COMPONENT-NONREACT			CAL WT	WT %
ACRAWAX C			11.68	0.250
IRGANOX 1010			11.68	0.250
Stabaxol P-200			23.36	0.500
			46.72	1.000
Totals for the Run			4671.91	100.000

10

Formulation for Figure 7 (DSC), No Crystallization Retarding  
Component=0 Equivalents

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	2.93	366.64	25.08
Butane diol (chain extender)	45.06	1.92	86.56	5.92
DPG Dipropylene Glycol (crc)	67.09	0.00	0.00	0.00
PTMEG 2000 (polyol)	1000.00	1.00	1000.00	68.40
TOTAL OH		2.92	1086.56	74.32
TOTAL OH & NCO			1453.20	99.40
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate (catalyst)			0.07	0.01
Acrawax C			0.00	0.00
IRGANOX 1010			4.39	0.30
Tinuvin 328			4.39	0.30
			8.85	0.61
TOTAL FOR RUN			1462.04	100.00

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Formulation for Figure 8 (DSC), 10 Equivalents of  
Crystallization Retarding Components per 100 OH Equivalents

COMPONENT-REACTIVE	EQ. Wt.	Equivalents	EqWt*EQ	WT %
MDI (polyisocyanate)	125.20	2.9410	368.21	24.967
Butane diol (chain extender)	45.06	1.6469	74.21	5.032
DPG Dipropylene Glycol (crc)	67.09	0.2941	19.73	1.338
PTMEG 2000 (polyol)	1000.00	1.0000	1000.00	67.808
TOTAL OH		2.9410	1093.94	74.178
TOTAL OH & NCO			1462.15	99.145
COMPONENT-NONREACT			CAL WT	WT %
Stannous Octoate (catalyst)			0.07	0.005
Acrawax C			3.69	0.250
IRGANOX 1010			4.42	0.300
Tinuvin 328			4.42	0.300
			12.61	0.855
TOTAL FOR RUN			1474.76	100.00

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Figure 1 shows the DSC scan of an ester TPU without DPG modifier. Relative rate of crystallization is indicated by the peak of crystallization temperature  $T_c$  at 121.6 °C and 136.2°C. the higher the peak temperature, the faster the crystallization rate is. The more perfect the crystal the higher the peak. In figure 2 this peak is reduced to 108.7°C by replacing 10% of total OH with DPG as chain extender. Also the relative intensity of the highest melting peak of the rescans (shown by the middle curve) can be used to anticipate potential extrusion problems. The larger and more intense this peak

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is, the more difficult will be the extrusion processability of TPU because of premature crystallization of the product inside the extruder. Figure 1 shows this peak at 222.4°C and more intense than the same peak in Figure 2 at 217.8°C. Analyzing the DSC curves of Figure 1 and Figure 2 we can therefore say that TPU in Figure 2 will be easier to extrude than TPU in Figure 1.

Applying the same analysis to the TPUs shown in Figure 3 through 8, we can surmise CRC modified TPU in Figures 4, 6, and 8 will extrude easier than unmodified TPU shown in Figures 3, 5, and 7 respectively.